

The effect of the size and structure of radicals on the rate of isomerization of esters of phosphorous acid.
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The nature of the Arbuzov reaction is discussed. Rumpf (Bull. Soc. Chim. France 129 C (1951)) suggests that the reaction is a chain reaction:

$$2 \text{P(OR)}_3 \rightarrow \text{RP}^+(\text{OR})_3 + \text{P(OR)}_2\text{O}^-; \text{RP}^+(\text{OR})_3 + \text{P(OR)}_3 \rightarrow \text{RP}^+(\text{OR})_2\text{O} + \text{RP}^+(\text{OR})_3 \text{ etc.}$$

In a similar chain sequence, P(OR)_3 can aid the loss of RX from the intermediate complex in each reaction link. The intermediates of the reaction can be regarded as phosphonium deriva. $(\text{RO})_3\text{PRX}$ (cf. Gerrard et al, J. Chem. Soc. 1951, 2550), which decompose thermally. The decompn. phase has been regarded as a bimolecular (Gerrard above) or monomolecular reaction (Pudovik, this j. 84, 519 (1952)), depending on the structure of R . The reaction can be regarded as being catalytic with RX being the catalyst. It can be regarded as being autocatalytic with the rate given by: $dx/dt = k(1 + nx)(1-x)$, where x is the relative concn. of the reaction product and n is a constant for a given expt. (cf. Zawidskii and Staronka (C.A. 11, 2294 (1917)); also Staronka, Chem. Centrallbl. 2, 366 (1927)).

In the present study several esters with trivalent P were prepd. These were: $(\text{PhO})_2\text{POMe}$, 56%, $b_{12} 165.5-6.5^\circ$, $d_{20}^{20} 1.1644$, $n_D^{20} 1.5528$; $(\text{PhO})_2\text{POEt}$, 60.5%, $b_{17.5} 182-3^\circ$, $d_{20}^{20} 1.1372$, $n_D^{23} 1.5475$; $(\text{PhO})_2\text{POCHMe}_2$, 58%, $b_{10} 170-1^\circ$, $d_{20}^{21} 1.1073$, $n_D^{21} 1.5394$; $(\text{PhO})_2\text{POBu}$, 52%, $b_{9.5} 187-7.5^\circ$, $d_{20}^{20} 1.0967$, $n_D^{20} 1.5370$; $(\text{PhO})_2\text{POCH}_2\text{CHMe}_2$, 68%, $b_9 180.5-1.0^\circ$, $d_{20}^{21} 1.0952$, $n_D^{21} 1.5358$; PhOP(OMe)_2 , 60.6%, $b_{9.6} 96-7^\circ$, $d_{20}^{21} 1.1267$, $n_D^{21} 1.5053$; PhOP(OEt)_2 , 35.3%, $b_{11} 113^\circ$, $d_{20}^{20} 1.0659$, $n_D^{20} 1.4933$; The esters were allowed to react with the corresponding alkyl iodides. It was found that a smooth reaction took place only with Me and Et esters. Higher homologs apparently were quite unreactive below 200° while at higher temps. decompn. occurred. The products obtained were: 93.5% MeP(O)(OMe)(OPh) , $b_{11} 135-6^\circ$, $d_{20}^{20} 1.1914$, $n_D^{20} 1.5054$; 84% EtP(O)(OEt)(OPh) , $b_{12.5} 142.5-3.5^\circ$, $d_{20}^{20} 1.1197$, $n_D^{20} 1.4922$; 88.3% MeP(O)(OPh)_2 .

$b_g 192-2.5^\circ$, $d_o^{20} 1.2058$, $n_D^{20} 1.5518$; 80% EtP(O)(OPh)_2 , $b_{13} 202^\circ$, $d_o^{20} 1.1799$, $n_D^{20} 1.5451$; 33.7% iso-PrP(O)(OPh)_2 , $b_{10.5} 198-200^\circ$, $d_o^{20} 1.1497$, $n_D^{20} 1.5383$; 52% BuP(O)(OPh)_2 , $b_{11} 205-7.5^\circ$, $d_o^{20} 1.1293$, $n_D^{20} 1.5339$; 35% iso-BuP(O)(OPh)_2 , $b_{11.5} 190-2^\circ$, $m. 104^\circ$; 76% $\text{PhCH}_2\text{P(O)(OPh)}_2$, $m. 66^\circ$. Adducts of ~~Me~~ alkyl iodides to $(\text{PhO})_3\text{P}$ were isolated in crystalline state (crystallized from $\text{Et}_2\text{O-ClCH}_2\text{CH}_2\text{Cl}$): 100% $(\text{PhO})_3\text{PCH}_2\text{PhI}$, $m. 112-14^\circ$; 100% $(\text{PhO})_3\text{PMeI}$, $m. 130^\circ$; 100% $(\text{PhO})_3\text{PEtI}$, $m. 89-91^\circ$; 12.1% $(\text{PhO})_3\text{PBuI}$, ~~unstated~~ unstated yield of crude; $(\text{PhO})_3\text{PCHMe}_2\text{I}$, 12.1%, $m. 110^\circ$; unstated yield of $(\text{PhO})_3\text{PCH}_2\text{CHMe}_2\text{I}$, $m. 157-7.5^\circ$. The reactions of these (PhCH_2 , iso-Pr , Bu , and iso-Bu derivs.) with EtOH readily gave the corresponding RP(O)(OPh)_2 listed above. Thermal decompn. of the adducts (Me , Et , iso-Pr , and Bu) at $210-230^\circ$ gave mainly the expected phosphonates, but also gave much tarry matter and considerable amounts of free iodine. A dilatometric examn. of the addn. of alkyl iodides to $(\text{PhO})_3\text{P}$ and the decompn. of the adducts was made to follow the reaction rates. The reactions of isomerization and addn. were shown to have a temp. coeff. of the reaction rate that was close to 2 (for 10° rise). The order the isomerization reactions, calcd. on the basis of the dilatometric curves, was variable and was always smaller than unity, but the reaction curves cannot be described by the sequence given by Staronka (cf. above). Replacement of Me in a phosphite by Et reduces the isomerization rate by some 30-40 fold; replacement of an aliphatic radical by Ph reduces the reaction rate 7-9 fold. PhCH_2I adds to $(\text{PhO})_3\text{P}$ most rapidly among the halides studied. The rate of addn. falls rapidly with increase of size of the alkyl. iso-PrI adds most slowly. Addn. of iso-BuI is 10 times faster than of BuI , but has a long induction period. The effect of the isomerization product on the rate of isomerization was examined with PhOP(OMe)_2 ; to equimolar mixture of this phosphite and MeI was added MeP(O)(OMe)(OPh) in different amounts and the reaction was run at 64.5° . Without such addn. the reaction

was 25% complete in 48 min., 50% in 86 min., 75% in 130 min. and 100% in 315 min.; with 0.2 moles phosphonate added it was 25% complete in 38 min, 50% in 71 min., 75% in 110 min, and 100% in 240 min.; with 0.5 mole phosphonate added the reaction was 25% complete in 34 min, 50% in 67 min., 75% in 107 min., and 100% in 230 min; with 1 mole phosphonate the reaction was 25% complete in 32 min., 50% in 62 min., 75% in 105 min., and 100% in 240 min. Thus a small autocatalytic effect might be active, although the alteration of the reaction medium can be the active principle.
